

## KINETICS OF THE OXIDATION OF ORGANODITIN COMPOUNDS BY SUBSTITUTED 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE AND 2,2',2''-TRIPYRIDINE COMPLEXES OF IRON(III)

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### Summary

The kinetics of the oxidation of some organoditin compounds by a number of substituted 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2''-tripyridine complexes of iron(III) have been investigated spectrophotometrically in acetonitrile. The reactions lead to the cleavage of the tin—tin bond with the concomitant reduction of two moles of the iron(III) complex per mole of organoditin compound reacted. The reactions obey a second-order rate law, first-order with respect to distannane and iron(III). The reactivity order of the organoditin compounds is  $\text{Ph}_6\text{Sn}_2 < \text{Me}_3\text{SnSnPh}_3 < \text{Me}_6\text{Sn}_2 < \text{Bu}_6\text{Sn}_2$  for every iron(III) complex. The reactivity order of the iron(III) complexes towards any given distannane parallels the order of the formal redox potentials of the complexes when the ligands bonded to iron(III) are 1,10-phenanthroline, 5-nitro-, 5-methyl-, 5,6-dimethyl-, or 3,4,7,8-tetramethyl-1,10-phenanthroline and bipyridine. For these a linear relationship between the free energy of activation and the standard free energy changes related to the actual electron-transfer step is observed, the slope (0.44) being in reasonably good agreement with the theoretical prediction for the proposed outer sphere redox mechanism.

### Introduction

In a previous paper [1] we reported a kinetic investigation of the oxidation of some organoditin compounds of the type  $\text{R}_6\text{Sn}_2$  ( $\text{Me}_6\text{Sn}_2$ ,  $\text{Me}_3\text{SnSnPh}_3$ ,  $\text{Ph}_6\text{Sn}_2$ ,  $\text{Bu}_6\text{Sn}_2$ ) by  $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$  (phen = 1,10-phenanthroline) in acetonitrile. We have now carried out a kinetic study on the oxidation of the same organoditin compounds by octahedral iron(III) complexes of substituted 1,10-phenanthroline [i.e. 5-nitro-1,10-phenanthroline (5- $\text{NO}_2$ phen), 5-methyl-1,10-phenanthroline (5-Mephen), 5,6-dimethyl-1,10-phenanthroline (5,6- $\text{Me}_2$ phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8- $\text{Me}_4$ phen), 4,7-diphenyl-1,10-phenanthroline (4,7- $\text{Ph}_2$ phen)], 2,2'-bipyridine (bipy) and 2,2',2''-tripyridine

(tripy) in acetonitrile. The purpose of this investigation was to evaluate how thermodynamics affect the rates of this kind of non-complementary reactions. It was hoped that the use of chelating ligands and R groups of different bulkiness would also provide information about the importance of steric hindrance in these reactions.

## Experimental

### *Materials*

Organoditin compounds were obtained and purified as described in the previous paper [1].

The iron(III) complexes were prepared either by oxidizing a solution of the iron(II) complex in dilute sulfuric acid with lead dioxide (for bipy, 5-Mephen, 5,6-Me<sub>2</sub>phen and 3,4,7,8-Me<sub>4</sub>phen) or by oxidizing a solution of the iron(II) complex in concentrated sulfuric acid with cerium(IV) (for tripy, 5-NO<sub>2</sub>phen and 4,7-Ph<sub>2</sub>phen). The parent iron(II) complexes were prepared in solution by adding an equivalent amount of the appropriate ligand to a solution of iron(II) sulfate. In the preparation of the complex with 4,7-Ph<sub>2</sub>phen, acetonitrile was added to the aqueous solution in order to increase the solubility of both the ligand and the complex. The iron(III) complexes were precipitated by adding NaClO<sub>4</sub> and were then filtered off. They were washed with dilute perchloric acid, dried under vacuum and kept in the dark under nitrogen. When filtration was difficult the precipitate was separated by centrifugation, and purified by dissolution in acetone followed by reprecipitation with diethyl ether.

Acetonitrile was purified and dried by standard methods [2].

### *Preparation of the reaction mixtures, stoichiometry of the reactions and evaluation of the reaction rates*

The experimental procedures described in the previous paper [1] were used. In particular, stock solutions of the iron(III) complexes were prepared by weight in blackened flasks, and used immediately after preparation, care being taken to avoid any contamination with atmospheric moisture. These solutions were usually stable for the time required to carry out the kinetic experiments. However, the complexes with tripy and 3,4,7,8-Me<sub>4</sub>phen were found to undergo a relatively fast decomposition so that for these the rate constants have been evaluated with a degree of uncertainty which did not allow the determination of the related activation parameters. Both iron(III) and iron(II) complexes exhibit absorption spectra which are very similar to those obtained when equimolar amounts of these complexes are dissolved in aqueous sulfuric acid. The reactions were followed spectrophotometrically by recording the absorption changes with time of the reaction mixtures at a wavelength where the iron(II) complex formed during the reaction exhibits an absorption maximum (i.e. 516 for 5-Mephen, 510 for 5-NO<sub>2</sub>phen, 512 for 5,6-Me<sub>2</sub>phen, 500 for 3,4,7,8-Me<sub>4</sub>phen, 533 for 4,7-Ph<sub>2</sub>phen, 522 for bipy and 552 nm for tripy). Slower reactions were followed by scanning the spectrum at appropriate times over a range of wavelengths which included the above-mentioned absorption maxima. The stoichiometry of the reactions was determined as previously described for the reactions of [Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> [1], and is consistent with eqn. 1. The

stoichiometry was not fully established for the reactions with the complexes of tripy and 3,4,7,8-Me<sub>4</sub>phen, owing to the instability of the starting iron(III)



complexes. However, it was found that with these two moles of iron(II) complex are also formed, in good approximation, per mole of organoditin reacted. The rate law and the rate constants were evaluated following the procedure described in the previous paper [1]. The concentration ranges used were:

(a) For 5-NO<sub>2</sub>phen: [Fe<sup>III</sup>]<sub>0</sub>, 2.50 × 10<sup>-5</sup>–4.00 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 9.35 × 10<sup>-5</sup>–3.50 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 1.00 × 10<sup>-4</sup>–2.50 × 10<sup>-4</sup> M;

(b) For 5-Mephen: [Fe<sup>III</sup>]<sub>0</sub>, 2.00 × 10<sup>-5</sup>–3.00 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 9.80 × 10<sup>-5</sup>–3.50 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 5.00 × 10<sup>-5</sup>–2.50 × 10<sup>-4</sup> M; [Me<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 7.75 × 10<sup>-5</sup>–2.33 × 10<sup>-4</sup> M; [Bu<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 6.20 × 10<sup>-5</sup>–2.48 × 10<sup>-4</sup> M;

(c) For 5,6-Me<sub>2</sub>phen: [Fe<sup>III</sup>]<sub>0</sub>, 1.50 × 10<sup>-5</sup>–2.50 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 9.80 × 10<sup>-5</sup>–3.50 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 4.65 × 10<sup>-5</sup>–2.34 × 10<sup>-4</sup> M; [Me<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 1.50 × 10<sup>-4</sup>–7.50 × 10<sup>-4</sup> M; [Bu<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 6.20 × 10<sup>-5</sup>–3.10 × 10<sup>-5</sup> M;

(d) For 3,4,7,8-Me<sub>4</sub>phen: [Fe<sup>III</sup>]<sub>0</sub>, 1.50 × 10<sup>-5</sup>–2.50 × 10<sup>-5</sup> M; [Me<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 1.40 × 10<sup>-4</sup>–5.00 × 10<sup>-4</sup> M; [Bu<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 1.40 × 10<sup>-4</sup>–5.00 × 10<sup>-4</sup> M;

(e) For 4,7-Ph<sub>2</sub>phen: [Fe<sup>III</sup>]<sub>0</sub>, 1.00 × 10<sup>-5</sup>–1.50 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 9.35 × 10<sup>-5</sup>–3.34 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 6.65 × 10<sup>-5</sup>–2.50 × 10<sup>-4</sup> M; [Me<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 1.07 × 10<sup>-4</sup>–4.00 × 10<sup>-4</sup> M; [Bu<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 6.20 × 10<sup>-5</sup>–3.10 × 10<sup>-4</sup> M;

(f) For bipy: [Fe<sup>III</sup>]<sub>0</sub>, 2.00 × 10<sup>-5</sup>–3.00 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 5.35 × 10<sup>-5</sup>–3.34 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 5.00 × 10<sup>-5</sup>–2.50 × 10<sup>-4</sup> M; [Me<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 1.00 × 10<sup>-4</sup>–5.00 × 10<sup>-4</sup> M; [Bu<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 6.25 × 10<sup>-5</sup>–2.50 × 10<sup>-4</sup> M;

(g) For tripy: [Fe<sup>III</sup>]<sub>0</sub>, 2.00 × 10<sup>-5</sup>–3.00 × 10<sup>-5</sup> M; [Ph<sub>6</sub>Sn<sub>2</sub>]<sub>0</sub>, 9.80 × 10<sup>-5</sup>–3.50 × 10<sup>-4</sup> M; [Me<sub>3</sub>SnSnPh<sub>3</sub>]<sub>0</sub>, 1.75 × 10<sup>-4</sup>–5.25 × 10<sup>-4</sup> M.

The reaction rates were evaluated at two temperatures (20 and 35°), with the exception of the complexes of tripy and 3,4,7,8-Me<sub>4</sub>phen for which rates at 20° only were obtained. At least seven kinetic runs were carried out at each temperature and for each system.

## Results and discussion

All the organoditin compounds examined undergo oxidation by iron(III) according to eqn. 1, following the second-order rate law (eqn. 2), which was previously found for the oxidation of the same distannanes by [Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> [1]. The values of *k*<sub>2</sub> are listed in Table 1 together with the related activation parameters. The reactivity changes observed on changing either the organoditin or the iron(III) complex are mainly caused by changes in only the enthalpy of activation. Only for the reactions of the asymmetric distannane does an additional entropy contribution seem to operate, possibly as a consequence of a statistical factor arising when the activated complex involves this compound of lower symmetry.

$$-\frac{d[Fe^{III}]}{dt} = k_2 \cdot [Fe^{III}] \cdot [R_6Sn_2] \quad (2)$$

The reactivity order of the organoditin compounds examined, Ph<sub>6</sub>Sn<sub>2</sub> < Me<sub>3</sub>SnSnPh<sub>3</sub> < Me<sub>6</sub>Sn<sub>2</sub> < Bu<sub>6</sub>Sn<sub>2</sub>, appears to be independent of the iron(III)

TABLE 1  
SECOND-ORDER RATE CONSTANTS,  $k_2$ , AND ACTIVATION PARAMETERS FOR THE OXIDATION OF ORGANODITIN COMPOUNDS BY IRON(II) COMPLEXES IN ACETONITRILE<sup>a</sup>

Complex	Organoditin compound	T (°C)	$k_2$ (l mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^*$ (kcal mol <sup>-1</sup> )	$\Delta S^*$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
[Fe(5-NO <sub>2</sub> phen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	35	$3.35 \times 10^3$	11.3	- 5
		20	$1.22 \times 10^3$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	35	$4.04 \times 10^4$	8.1	-11
		20	$1.95 \times 10^4$		
[Fe(5-Mephen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	35	$6.57 \times 10^1$	13.6	- 6
		20	$2.00 \times 10^1$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	35	$1.09 \times 10^3$	10.5	-12
		20	$4.28 \times 10^2$		
	Me <sub>6</sub> Sn <sub>2</sub>	35	$3.30 \times 10^4$	9.0	- 9
		20	$1.48 \times 10^4$		
	Bu <sub>6</sub> Sn <sub>2</sub>	35	$1.03 \times 10^5$	8.0	-10
		20	$5.02 \times 10^4$		
[Fe(5,6-Me <sub>2</sub> phen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	35	$4.27 \times 10^1$	12.9	- 9
		20	$1.38 \times 10^1$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	35	$6.25 \times 10^2$	9.7	-14
		20	$2.63 \times 10^2$		
	Me <sub>6</sub> Sn <sub>2</sub>	35	$2.29 \times 10^4$	8.6	-11
		20	$1.06 \times 10^4$		
	Bu <sub>6</sub> Sn <sub>2</sub>	35	$6.36 \times 10^4$	8.3	-10
		20	$3.02 \times 10^4$		
[Fe(3,4,7,8-Me <sub>4</sub> phen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Me <sub>6</sub> Sn <sub>2</sub>	20	$3.3 \times 10^{2b}$		
	Bu <sub>6</sub> Sn <sub>2</sub>	20	$1.3 \times 10^{3b}$		
[Fe(4,7-Ph <sub>2</sub> phen) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	35	$5.79 \times 10^1$	13.7	- 6
		20	$1.76 \times 10^1$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	35	$9.94 \times 10^2$	10.0	-12
		20	$4.10 \times 10^2$		
	Me <sub>6</sub> Sn <sub>2</sub>	35	$2.69 \times 10^4$	8.4	-11
		20	$1.26 \times 10^4$		
	Bu <sub>6</sub> Sn <sub>2</sub>	35	$1.02 \times 10^5$	8.2	- 9
		20	$4.86 \times 10^4$		
[Fe(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	35	$4.90 \times 10^1$	13.7	- 6
		20	$1.49 \times 10^1$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	35	$8.20 \times 10^2$	10.1	-12
		20	$3.34 \times 10^2$		
	Me <sub>6</sub> Sn <sub>2</sub>	35	$2.48 \times 10^4$	8.9	-10
		20	$1.12 \times 10^4$		
	Bu <sub>6</sub> Sn <sub>2</sub>	35	$6.12 \times 10^4$	8.6	- 9
		20	$2.82 \times 10^4$		
[Fe(tripy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Ph <sub>6</sub> Sn <sub>2</sub>	20	$1.1 \times 10^{2b}$		
	Me <sub>3</sub> SnSnPh <sub>3</sub>	20	$1.8 \times 10^{3b}$		

<sup>a</sup>Errors:  $k_2$ ,  $\pm$  3%;  $\Delta H^*$ ,  $\pm$  1 kcal mol<sup>-1</sup>;  $\Delta S^*$ ,  $\pm$  3 cal K<sup>-1</sup> mol<sup>-1</sup>. <sup>b</sup> $\pm$  20%.

complex considered. A similar trend has been previously found also for the reactions of these distannanes with [Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> [1]. In such a case the log  $k_2$  values of the different organoditin compounds were found to be linearly correlated with the sum of the Taft  $\sigma^*$  values ( $\Sigma\sigma^*$ ) of the R groups bonded to

the tin atoms, showing that the relative tendency of the tin atoms to donate electrons is a primary effect in determining the above reactivity trend [1]. A similar relationship is now found for the reactions with the iron(III) complexes examined in this paper, so that the reactivity of a single iron(III) complex with a single organoditin compound, at a given temperature, can be expressed by relationship 3, where  $C_L$  is a constant whose value depends only upon the

$$\log k_2 = -1.29 \Sigma\sigma^* + C_L \quad (3)$$

ligand bonded to iron(III), and  $\Sigma\sigma^*$  has the meaning assigned above. The occurrence of a constant slope in relationship 3, whichever iron(III) complex is considered (see Fig. 1), suggests that the ligands bonded to iron(III) do not exhibit any discriminating steric effect on the reaction rate. The absence of a specific steric effect had been found previously for other redox reactions involving either the reduction of iron(III)—phenanthroline complexes or the oxidation of the related iron(II) complexes [3–6]. In the reduction of these complexes by iron(II) ions [3] such behaviour was ascribed to the formation of an activated complex in which the iron(II) ion had penetrated the space between the phenanthroline groups of the iron(III) complex. Such an interpretation hardly explains the absence of any discriminating steric effect for the reactions with organoditin

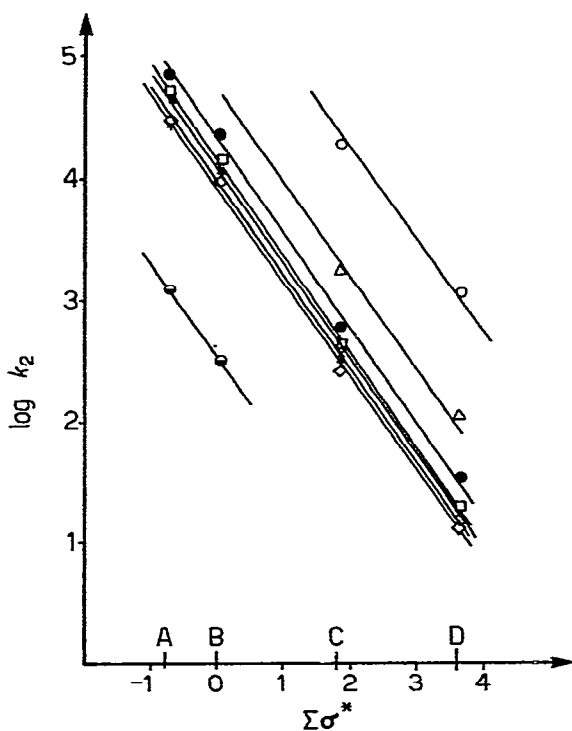


Fig. 1. Relationship between  $\Sigma\sigma^*$  and  $\log k_2$  for the oxidation of  $\text{Bu}_6\text{Sn}_2$  (A),  $\text{Me}_6\text{Sn}_2$  (B),  $\text{Me}_3\text{SnSnPh}_3$  (C), and  $\text{Ph}_6\text{Sn}_2$  (D) by iron(III) complexes in acetonitrile at  $20^\circ$ . Chelating agents: 5- $\text{NO}_2$ phen (○), tripy (△), phen (●), 5-Mephen (□), 4,7- $\text{Ph}_2$ phen (×), 5,6- $\text{Me}_2$ phen (◇), bipy (+), 3,4,7,8- $\text{Me}_4$ phen (⊙). Data for phen taken from ref. 1.

compounds since these bulky distannanes appear to have little possibility of penetrating the space between the phenanthroline groups (or the other ligands) in the activated complex. On the other hand the reactivity sequence of the iron(III) complexes relative to any given organoditin compound does not follow the degree of steric hindrance of the ligands bonded to iron(III), as can be seen from the sequence of the values of  $C_L$  at 20°. Reactivity sequence ( $C_L$ ): 5-NO<sub>2</sub>phen (5.75) > tripy (4.71) > phen (4.22\*) > 5-Mephen (4.04) ≈ 4,7-Ph<sub>2</sub>phen (4.00) > bipy (3.89) ≈ 5,6-Me<sub>2</sub>phen (3.86) > 3,4,7,8-Me<sub>4</sub>phen (2.34).

Thus it appears that the most likely reaction mechanism is an outer sphere redox mechanism involving an activated complex in which the oxidant and the reductant are arranged such that the relative steric hindrance of the ligands bonded to iron(III) gives rise to a negligible kinetic effect. A similar conclusion was previously reached by considering the role played by the R groups bonded to the tin atoms in affecting the reaction rates [1]. The above mechanism would be consistent with a previous suggestion that in such redox processes the reactants do not approach closely before the electron transfer [1]. A mechanism which can account for the above conclusions and the observed stoichiometry and rate law is described by equations 4a–d, the rate determining step 4a being an outer sphere redox path.



In agreement with the theoretical predictions [7,8], the reactivity sequence outlined above appears to be primarily related to the thermodynamic tendency of the iron(III) complexes to accept an electron, rather than to steric requirements. In fact, it is found (Fig. 2) that the values of  $\log k_2$  for the reduction of iron(III) complexes by the same organoditin compound are linearly correlated with the formal redox potential,  $E^{0'}(Fe^{III}/Fe^{II})$  of the iron complexes under examination<sup>\*\*</sup>, except the tripy and 4,7-Ph<sub>2</sub>phen complexes.

A direct correlation between the free energy of activation and the standard free energy changes for the actual electron-transfer step 4a is not possible because  $\Delta G^{0'}$  is not evaluable. However, for a series of reactions in which the distannane is kept constant, one finds that  $\Delta G^{0'}$  is a function of  $E^{0'}(Fe^{III}/Fe^{II})$ :

$$\begin{aligned} \Delta G^{0'} &= 0.239 \times 96.5 [E^{0'}(Fe^{III}/Fe^{II}) - E^{0'}(R_6Sn_2 \cdot^+/R_6Sn_2)] \\ &= 23 E^{0'}(Fe^{III}/Fe^{II}) + C \text{ (kcal mol}^{-1}\text{)} \end{aligned} \quad (5)$$

\* Data taken from ref.1.

\*\* The formal redox potentials are not known in acetonitrile, but they are believed to be essentially the same as those exhibited in water [9]. The values used in this paper refer to 1 F H<sub>2</sub>SO<sub>4</sub> solutions [3] but the difference between these values and those for pure water, when known, are relatively small and roughly independent of the complex considered [10], so that the correlations of Fig. 2 still hold.

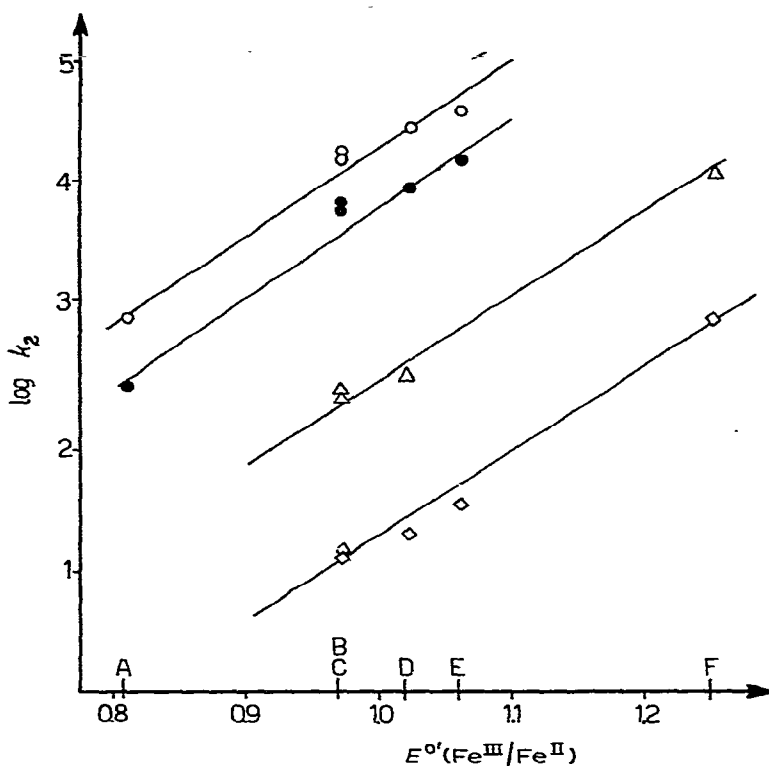


Fig. 2. Relationship between  $\log k_2$  values for the oxidation of  $\text{Bu}_6\text{Sn}_2$  ( $\circ$ ),  $\text{Me}_6\text{Sn}_2$  ( $\bullet$ ),  $\text{Me}_3\text{SnSnPh}_3$  ( $\Delta$ ) and  $\text{Ph}_6\text{Sn}_2$  ( $\diamond$ ) by various iron(III) complexes, in acetonitrile at  $20^\circ$ , and the formal redox potentials of the iron complexes. Chelating agents: 3,4,7,8- $\text{Me}_4\text{phen}$  (A), bipy (B), 5,6- $\text{Me}_2\text{phen}$  (C), 5- $\text{Mephen}$  (D), phen (E), 5- $\text{NO}_2\text{phen}$  (F). Data for phen taken from ref. 1.

Thus, information on the relationship between  $\Delta G^*$  and  $\Delta G^{0'}$  can be obtained by plotting the values of the free energy of activation against  $23 E^{0'}(\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}})$ . Linear relationships between  $\Delta G^*$  and  $\Delta G^{0'}$  are found when such plots are made for the four series of reactions and in each case the slope is ca. 0.44, a value which is in reasonably good agreement with the theoretical value of 0.5 expected for a series of similar outer sphere redox reactions [7].

The 2,2',2''-tripyridine complex [ $E^{0'}(\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}) = 0.93 \text{ V}$ ] reacts approximately fifteen times more quickly than would be expected on the basis of its formal redox potential, whereas, the 4,7-diphenyl-1,10-phenanthroline complex [ $E^{0'}(\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}) = 1.25 \text{ V}$ ] reacts nearly sixty times more slowly. Such apparently anomalous behavior for these two complexes appears to be rather general in view of the fact that similar anomalies have been encountered by other authors in the reduction of the iron(III) complexes under examination by iron(II) ions [3]. A satisfactory explanation of these anomalies is not possible at the present time. However, theory predicts [7] that the free energy of activation of the electron-transfer process,  $\Delta G^*$ , is dependent on the free energy of activation of the electron exchange reaction between the iron(III) and iron(II) complexes involved in the electron-transfer step,  $\Delta G^*(\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}})$ , so that the mentioned

anomalies could be the consequence of a different value of  $\Delta G^*(\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}})$  for the complexes containing trip $\pi$  and 4,7-Ph $_2$ phen, compared with a roughly constant value for the other iron complexes examined.

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